compounds have bidentate ligands which may obscure electronic site preferences.[4g]

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Registry No. **1**, 61916-34-5; **2**, 61916-35-6; **3**, 61916-36-7; **4**, 61916-37-8; **5**, 61966-89-0; **6**, 61916-23-2; **7**, 50600-13-0; **8**, 61916-24-3; $(dmpe)_2Ta(CO)_2D$, 61916-25-4; $(dmpe)_2Ta(CO)_2(CF_3CO_2)$, 61916-26-5; $TaCl_5$, 7721-01-9.

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Comparative Geometry of $Rh(\mu\text{-}Cl)_2Rh$ and $Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ Bridges. Crystal Structure of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ and Its Relationship to $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$

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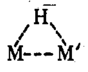
A single-crystal x-ray diffraction study has been performed on the complex di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium, $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$. This species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 8.375$ (1) Å, $b = 9.228$ (2) Å, $c = 15.651$ (2) Å, $\beta = 106.70$ (1)°, and $V = 1158.6$ (3) Å^3 at 22 °C. Observed and calculated densities are 1.764 (10) and 1.772 g cm^{-3} for mol wt 618.08 and $Z = 2$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 2.57\%$ and $R_{wF} = 3.47\%$ for 1513 symmetry-independent reflections in the range $4° < 2\theta \leq 45°$ (Mo Kα radiation). The molecule has crystallographic C_i ($\bar{1}$) symmetry with a planar $Rh(\mu\text{-}Cl)_2Rh$ bridge in which Rh···Rh = 3.7191 (6) Å, Rh–ClB = 2.452 (1) and 2.465 (1) Å, Rh–ClB–Rh′ = 98.29 (3)°, and ClB–Rh–ClB′ = 81.71 (3)°. The central $Rh(\mu\text{-}Cl)_2Rh$ bridge is compared with the $Rh(\mu\text{-}Cl)(\mu\text{-}H)Rh$ bridge in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)(\mu\text{-}H)$ with a view toward assessing bonding characteristics in a nonstressed $M(\mu_2\text{-}H)M$ system within a binuclear species.

Introduction

The structural characterization of transition metal complexes containing bridging hydride ligands has been an area of considerable interest for the last few years. We have recently summarized the results of x-ray (and neutron) diffraction studies on these species.[1] It is now generally agreed that a bent $M(\mu_2\text{-}H)M'$ system contains a "closed" two-electron three-center bond—i.e., that there is both direct metal–hydrogen bonding and a direct metal–metal bonding interaction within this system. We have suggested that such a system be represented by I.

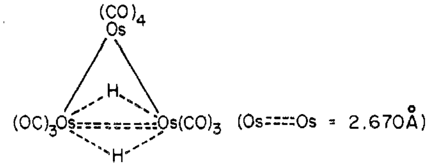


I

Mason and Mingos[2] have surveyed the geometry of binuclear and polynuclear complexes with bridging ligands and have noted that "electron-deficient" species (i.e., those with bridging ligands with only one pair of electrons available for bonding—hydride, alkyl, and aryl ligands, inter alia) have shorter metal–metal distances than do "electron-precise" species (i.e., those containing bridging ligands with at least two electron pairs available for bonding).

However, the only direct comparisons of complexes with bridging hydride ligands with their corresponding "electron-precise" analogues involves a trio of trinuclear osmium carbonyl species[2,3]—viz., $Os_3(CO)_{10}(\mu\text{-}H)_2$ (II), $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SEt)$[4] (III), and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ (IV).

While there is an obvious lengthening of the bis(μ_2-bridged) osmium–osmium vector as hydride ligands are successively replaced by "electron-precise" ligands, the bond under investigation may be subject to some additional constraints from the bridging $-Os(CO)_4-$ moiety. Thus, in order to isolate the effects of replacement of the μ_2-hydride ligand from other



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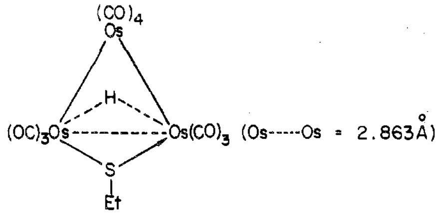

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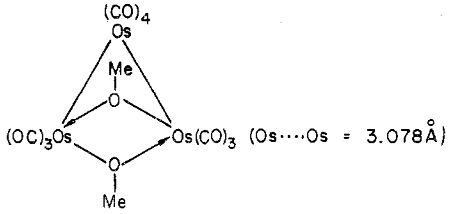
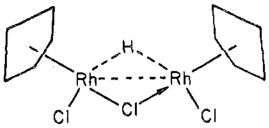


IV

possible steric effects, one must restrict his attention to binuclear species.

We have previously reported the results of an x-ray structural investigation of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$,[5] V,

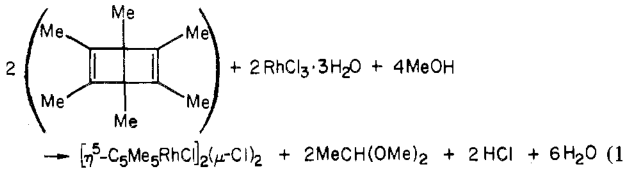


V

and we now report the results of a crystallographic study on the analogous "electron-precise" species $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$.

Experimental Section

$[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ was prepared by the method of Maitlis et al,[6] from the reaction of $RhCl_3\cdot3H_2O$ and hexamethyl(Dewar benzene) in methanol—see eq 1. The red solid thus obtained was



(1)

washed with ether, and contaminants were removed under vacuum. Crystals obtained from chloroform/benzene were found to crumble easily and were not satisfactory for single-crystal diffraction work. Suitable crystals were afforded by recrystallization from 1,2-dichloroethane. Most crystals were platelike but a crystal of approximately square cross section and dimensions 0.10 mm × 0.12 mm × 0.28 mm was selected for the single-crystal x-ray structural analysis. The crystal was mounted along its extended direction on the tip of a thin glass fiber which was then sealed into a 0.2 mm-diameter glass capillary and fixed into a eucentric goniometer. The crystal was accurately centered in a random orientation (later found to be with $[82\bar{3}]$ offset by ~1.2° from coincidence with the ϕ axis) on a Syntex $P2_1$ four-circle automated diffractometer under the control of a NOVA 1200 computer.

Measurement of unit cell parameters, determination of the orientation matrix, checks on peak profile, and data collection were carried out as described previously.[7] Details are given in Table I.

An examination of the data set revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with space group $P2_1/c$.[8] Systematically absent reflections were rejected. (None was observable at a 2σ level of significance.)

Table I. Data for the X-Ray Diffraction Study of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$

(A) Crystal Data[a]

Crystal system: monoclinic	$V = 1158.6\ (3)$ Å^3
Space group: $P2_1/c$ [C_{2h}^5; No. 14]	$T = 22$ °C
$a = 8.375$ (1) Å	$Z = 2$
$b = 9.228$ (2) Å	Mol wt 618.08
$c = 15.651$ (2) Å	ρ(obsd)[b] $= 1.764$ (10) g cm^{-3}
$\beta = 106.70$ (1)°	ρ(calcd) $= 1.772$ g cm^{-3}

(B) Collection of Intensity Data

Radiation: Mo Kα
Monochromator: highly oriented graphite, equatorial geometry
Monochromator angle: 12.2°
Takeoff angle: 6.9°
Reflections measd: $+h$, $+k$, $\pm l$
Max 2θ: 45°
Min 2θ: 4°
Scan type: coupled θ(crystal)-2θ(counter)
Scan speed: variable, 2.0-8.0°/min
Scan range: symmetrical, from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
Background measurement: Stationary crystal, stationary counter at beginning and end of scan; each for half the time taken for the scan
Std reflections: three remeasured after every 57 reflections; max deviations from the mean were 0.44% (1.9σ) for 004, 1.14% (4.2σ) for 040, and 0.76% (3.3σ) for 200
Reflections collected: 1850 total, 1515 independent

(C) Treatment of Intensity Data
"Ignorance factor": $p = 0.03$
Absorption coeff:[c] $\mu = 18.73$ cm^{-1}

[a] Unit cell parameters are from a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ peaks ($\bar{\lambda}$ 0.710 730 Å) of 15 reflections with $2\theta = 21.7\text{-}28.9°$. [b] The density was measured by neutral buoyancy in aqueous BaI_2. [c] All reflections in the range $h = 0 \rightarrow 2$, $k = 0 \rightarrow 2$, $l = -2 \rightarrow +2$ were measured at 10° intervals of ψ (the azimuthal angle, corresponding to rotation of the crystal about its diffraction vector) from $\psi = 0°$ to $\psi = 350°$, except when such measurements were geometrically inaccessible. The average deviation of the intensity from its mean value was 3% in F^2, indicating that absorption corrections could safely be ignored.

Solution and Refinement of the Structure

All calculations were performed on the CDC 6400 computer at SUNY at Buffalo. Programs used include JIMDAP (Fourier synthesis), LINEX74 (structure factor calculation and least-squares refinement), ORFFE (distances and angles with esd's), PLOD (least-squares planes), and ORTEP (thermal ellipsoids).

Scattering factors for neutral Rh, Cl, and C were taken from the compilation of Cromer and Waber;[9] the Stewart values for a "floated spherical H atom" were used.[10] Real and imaginary components of anomalous dispersion were included for all nonhydrogen atoms, using the values tabulated by Cromer and Liberman.[11]

The function $\sum w(|F_o| - |F_c|)^2$ (where $w = \sigma^{-2}(F_o)$) was minimized during least-squares refinement. Discrepancy indices R_F and R_{wF} are defined

$$R_F = \left[\frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The approximate scale factor and overall temperature factor were determined from a Wilson plot. The position of the (single independent) rhodium atom was quickly ascertained from a three-dimensional Patterson map. The locations of the remaining 12 nonhydrogen atoms were determined from a series of Fourier syntheses, each being phased by an increasing number of atoms. Refinement of the scale factor and positional and isotropic thermal parameters for all nonhydrogen atoms (53 variables) led to convergence with $R_F = 10.2\%$ and $R_{wF} = 15.1\%$. Continued refinement using anisotropic thermal parameters for all nonhydrogen atoms (118 variables) converged with reduced residuals of $R_F = 3.61\%$ and $R_{wF} = 6.31\%$.

Table II. Positional Parameters with Esd's for Atoms in the $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ Molecule[a,b]

Atom	x	y	z
Rh	0.189 320 (29)	0.032 610 (28)	0.094 917 (16)
ClB	0.108 37 (12)	0.017 36 (11)	−0.069 19 (6)
ClT	0.251 30 (14)	−0.221 22 (11)	0.111 02 (8)
C(1)	0.233 6 (6)	0.258 5 (4)	0.106 9 (3)
C(2)	0.189 6 (5)	0.205 6 (5)	0.184 5 (3)
C(3)	0.316 0 (4)	0.102 2 (4)	0.226 0 (2)
C(4)	0.430 3 (4)	0.098 0 (4)	0.176 2 (2)
C(5)	0.381 8 (5)	0.189 0 (4)	0.104 2 (2)
C(6)	0.140 5 (11)	0.372 2 (7)	0.042 2 (7)
C(7)	0.044 3 (8)	0.250 5 (11)	0.215 4 (7)
C(8)	0.330 3 (10)	0.019 4 (9)	0.311 2 (4)
C(9)	0.586 8 (7)	0.002 3 (8)	0.203 0 (5)
C(10)	0.475 2 (8)	0.212 0 (8)	0.034 7 (4)

[a] Esd's, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [b] The asymmetric unit consists of half of an $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ molecule. Atoms in the "other half" of the molecule are identified in the text by a prime and are related to those of the basic asymmetric unit by the transformation $(x', y', z') = (-x, -y, -z)$.

A difference-Fourier synthesis revealed some evidence of the methyl hydrogens (peak heights 0.6 → 0.2 e Å^{-3}) in reasonable positions and these were now included in the calculations. Continued refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for the hydrogen atoms led to final convergence with R_F = 2.57% and R_{wF} = 3.47%. The "goodness-of-fit", defined by $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, was 1.70. Here n is the number of observations (1513) and m is the number of variables (178); the ratio $n{:}m$ was 8.5:1. The function $\sum w(|F_o| - |F_c|)^2$ was not markedly dependent either upon $|F_o|$ or upon $(\sin \theta)/\lambda$, indicating that the weighting scheme is acceptable.

The correctness and completeness of the structural analysis were confirmed by a final difference-Fourier synthesis, on which the highest peak was of height 0.52 e Å^{-3} (at 0.00, 0.36, 0.015).

Final positional parameters are collected in Table II; anisotropic thermal parameters are listed in Table III.

The Molecular Structure

Intramolecular distances and angles are shown in Tables IV and V, respectively. Least-squares planes are given in Table VI.

As expected, the molecule consists of two $[\eta^5\text{-}C_5Me_5RhCl]$ units bridged by two μ_2-chloride ligands. The molecule has precise (i.e., crystallographically required) C_i ($\bar{1}$) symmetry. As shown in Figure 1, atoms in the basic asymmetric unit are labeled normally, while atoms in the "other half" of the molecule, which is related to the basic unit by the transformation $(x', y', z') = (-x, -y, -z)$, are labeled with a prime.

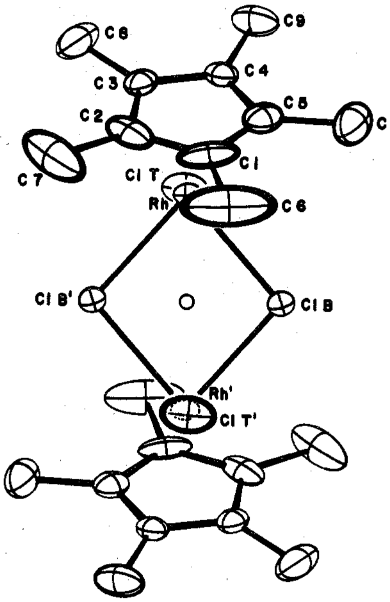


Figure 1. The $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)$ molecule, projected onto its $Rh(\mu\text{-}Cl)_2Rh$ plane. The center of symmetry is indicated by a hollow circle. Hydrogen atoms are omitted for the sake of clarity (ORTEP diagram; 30% ellipsoids).

The rhodium atom may be regarded as in an oxidation state of +3 (d^6 configuration); it achieves the expected noble gas configuration by the donation of six electrons from a $[\eta^5\text{-}C_5Me_5^-]$ anion and two electrons from each of three chloride ligands (ClT, ClB, and ClB′). The coordination geometry of the rhodium(III) atom is that loosely referred to as a "three-legged piano stool". Angles between the chloride ligands are ClB–Rh–ClB′ = 81.71 (3)°, ClB–Rh–ClT = 92.30 (4)°, and ClB′–Rh–ClT = 90.73 (4)°. The rotational orientation of the $RhCl_3$ group relative to the $[\eta^5\text{-}C_5Me_5]$ ligand is shown in Figure 2.

The terminal chloride ligand is slightly closer to the rhodium atom than are the bridging chloride ligands (Rh–ClT = 2.3967 (11) Å vs. Rh–ClB = 2.4649 (11) Å and Rh–ClB′ = 2.4522 (10) Å); the mean difference is, however, only ca. 0.062 Å.

Individual rhodium–carbon bond distances range from Rh–C(1) = 2.116 (4) Å to Rh–C(4) = 2.140 (3) Å, the average value being 2.128 Å. Although there is substantial librational motion of the $[C_5Me_5]$ ligand about its fivefold axis (cf. Figure 2), bond lengths within the system are not unreasonable. Carbon–carbon distances within the carbocyclic ring range from C(4)–C(5) = 1.370 (5) Å to C(1)–C(2) = 1.452 (7) Å, averaging 1.412 Å, as compared to the accepted C–C(π-cyclopentadienyl) distance of approximately 1.43 Å.[12] C(ring)–Me bond distances are not so adversely affected by libration and vary over a smaller range: from C(2)–C(7) = 1.492 (7) Å to C(4)–C(9) = 1.536 (7) Å, with an average value of 1.515 Å (i.e., indistinguishable from the accepted

Table III. Thermal Parameters[a] for Atoms in the $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ Molecule

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.0290 (2)	0.0283 (3)	0.0287 (2)	0.0003 (1)	−0.0010 (1)	−0.0034 (1)
ClB	0.0368 (5)	0.0592 (6)	0.0331 (5)	−0.0095 (4)	0.0095 (4)	−0.0098 (4)
ClT	0.0615 (7)	0.0324 (6)	0.0797 (8)	0.0056 (5)	−0.0082 (5)	−0.0005 (5)
C(1)	0.083 (3)	0.023 (2)	0.060 (3)	−0.002 (2)	−0.036 (2)	−0.003 (2)
C(2)	0.037 (2)	0.070 (3)	0.094 (3)	−0.007 (2)	0.009 (2)	−0.062 (3)
C(3)	0.047 (2)	0.048 (2)	0.034 (2)	−0.011 (2)	0.003 (2)	−0.008 (2)
C(4)	0.035 (2)	0.050 (2)	0.043 (2)	−0.006 (2)	0.001 (2)	−0.011 (2)
C(5)	0.056 (2)	0.046 (2)	0.046 (2)	−0.016 (2)	0.002 (2)	−0.008 (2)
C(6)	0.154 (8)	0.029 (3)	0.160 (8)	0.014 (3)	−0.082 (7)	−0.001 (4)
C(7)	0.061 (4)	0.173 (9)	0.215 (11)	−0.020 (4)	0.049 (5)	−0.150 (9)
C(8)	0.122 (6)	0.109 (6)	0.042 (3)	−0.048 (5)	0.009 (3)	−0.002 (3)
C(9)	0.049 (3)	0.084 (4)	0.083 (4)	0.015 (3)	−0.009 (3)	−0.006 (4)
C(10)	0.106 (4)	0.105 (4)	0.062 (3)	−0.054 (4)	0.032 (3)	−0.010 (3)

[a] The anisotropic thermal parameter is defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table IV. Interatomic Distances (A) with Esd's for $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$[a]

	(a) Distances within $ClRh(\mu\text{-}Cl)_2RhCl$ Core		
Rh···Rh'	3.7191 (6)	ClB···ClB'	3.2166 (19)
Rh–ClB	2.4649 (11)	Rh'–ClB'	2.4649 (11)
Rh–ClB'	2.4522 (10)	Rh'–ClB	2.4522 (10)
Rh–ClT	2.3967 (11)	ClB···ClT	3.5063 (15)
		ClB···ClT'	3.4508 (15)
	(b) Other Distances from Rhodium		
Rh–C(1)	2.116 (4)	Rh···C(6)	3.237 (7)
Rh–C(2)	2.124 (4)	Rh···C(7)	3.224 (6)
Rh–C(3)	2.121 (3)	Rh···C(8)	3.251 (6)
Rh–C(4)	2.140 (3)	Rh···C(9)	3.284 (5)
Rh–C(5)	2.137 (4)	Rh···C(10)	3.265 (5)
	(c) Carbon–Carbon Distances within C_5Me_5 Ligand		
C(1)–C(2)	1.452 (7)	C(1)–C(6)	1.510 (8)
C(2)–C(3)	1.434 (6)	C(2)–C(7)	1.492 (7)
C(3)–C(4)	1.398 (5)	C(3)–C(8)	1.511 (7)
C(4)–C(5)	1.370 (5)	C(4)–C(9)	1.536 (7)
C(5)–C(1)	1.408 (6)	C(5)–C(10)	1.527 (6)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. Their calculation, via ORFFE, included the effects of uncertainties in the unit cell parameters as well as all elements of the correlation matrix. No corrections have been applied for the possible effects of thermal motion.

Table V. Interatomic Angles (deg) with Esd's for $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$

	(a) Angles within $Rh(\mu\text{-}Cl)_2Rh$ Bridge		
ClB–Rh–ClB'	81.71 (3)	ClB–Rh'–ClB'	81.71 (3)
Rh–ClB–Rh'	98.29 (3)	Rh–ClB'–Rh'	98.29 (3)
	(b) Other Angles around Rhodium		
ClB–Rh–ClT	92.30 (4)	Rh'···Rh–ClB	40.73 (2)
ClB'–Rh–ClT	90.73 (4)	Rh'···Rh–ClB'	40.98 (2)
	(c) Internal C–C–C Angles of C_5Me_5 Ligand		
C(5)–C(1)–C(2)	108.0 (3)	C(3)–C(4)–C(5)	110.7 (3)
C(1)–C(2)–C(3)	105.7 (3)	C(4)–C(5)–C(1)	108.1 (4)
C(2)–C(3)–C(4)	107.5 (4)		
	(d) External C–C–C Angles		
C(6)–C(1)–C(2)	126.1 (7)	C(8)–C(3)–C(4)	125.8 (5)
C(6)–C(1)–C(5)	125.9 (7)	C(9)–C(4)–C(3)	122.1 (5)
C(7)–C(2)–C(1)	127.2 (7)	C(9)–C(4)–C(5)	127.2 (5)
C(7)–C(2)–C(3)	127.1 (7)	C(10)–C(5)–C(4)	125.4 (4)
C(8)–C(3)–C(2)	126.6 (5)	C(10)–C(5)–C(1)	126.5 (5)

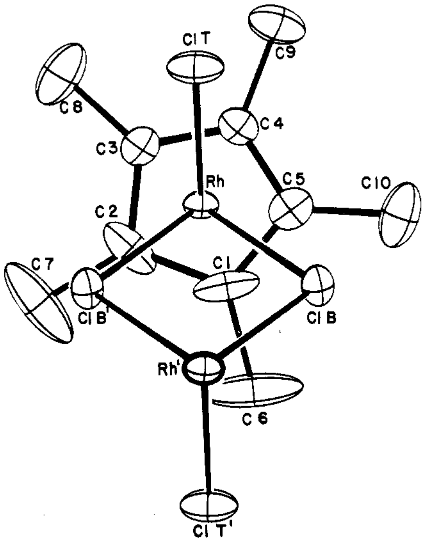


Figure 2. A portion of the $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ molecule, projected onto its carbocyclic ring (ORTEP diagram; 30% ellipsoids).

Table VI. Least-Squares Planes and Deviations of Atoms Therefrom[a,b]

Atom	Dev, Å	Atom	Dev, Å
Plane 1:	$-0.180\,58X + 0.981\,70Y - 0.060\,56Z = 0.0000$		
Rh*	0.000	ClB'*	0.000
Rh'*	0.000	ClT	−2.368
ClB*	0.000	ClT'	2.368
Plane 2:	$0.390\,37X + 0.734\,64Y + 0.554\,90Z = 3.2187$		
C(1)*	−0.001 (5)	C(6)	0.041 (9)
C(2)*	0.006 (5)	C(7)	0.039 (10)
C(3)*	−0.009 (4)	C(8)	0.035 (8)
C(4)*	0.009 (4)	C(9)	0.048 (7)
C(5)*	−0.005 (4)	C(10)	−0.001 (7)
Rh	−1.7558 (3)		

[a] Equations of planes are expressed in orthonormal coordinates (*X, Y, Z*) which are related to fractional coordinates (*x, y, z*) by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[b] Atoms marked with an asterisk were assigned unit weight; all others were given zero weight.

Table VII. Comparison of Selected Intramolecular Parameters of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ and $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$

	$Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ complex[a]	$Rh(\mu\text{-}Cl)_2Rh$ complex
Molecular symmetry	C_2	C_i
Rh···Rh', Å	2.9064 (10)	3.7191 (6)
Rh–Cl(bridging), Å	2.4374 (17)	2.4522 (10) 2.4649 (11)
Rh–H(bridging), Å	1.849 (47)	
Rh–ClB–Rh', deg	73.20 (6)	98.29 (3)
Rh–HB–Rh', deg	103.6 (37)	
ClB–Rh–X, deg	91.6 (18) (X = HB)	81.71 (3) (X = ClB')
Rh–ClT, Å	2.3929 (17)	2.3967 (11)

[a] See ref 5.

$C(sp^2)$–$C(sp^3)$ distance of 1.510 ± 0.005 Å).[13]

The rhodium atom lies −1.7558 Å from the least-squares plane through the five-membered carbocyclic ring; the methyl substituents, on average, bend *away* from the rhodium atom (individual displacements are +0.041 Å for C(6), +0.039 Å for C(7), +0.035 Å for C(8), +0.048 Å for C(9), and −0.001 Å for C(10)).

The $Rh(\mu\text{-}Cl)_2Rh$ Bridge Compared to the $Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ Bridge

The geometry of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$[5] and that for the present $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ molecule are compared in Table VII. Important differences are as follows.

1. The (nonbonding) Rh···Rh distance in the $Rh(\mu\text{-}Cl)_2Rh$ bridge is 3.7191 (6) Å—a value 0.8127 (12) Å longer than the Rh···Rh distance of 2.9064 (10) Å in the $Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ bridge. This difference is far greater than that of 0.215 Å found between the mono- and nonhydrido-bridged triosmium species $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SEt)$ (III) and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ (IV) and, indeed, is even greater than the difference of 0.408 Å between the dihydrido-bridged species $Os_3(CO)_{10}(\mu\text{-}H)_2$ (II) and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$. This confirms our belief that the quantitative effects of bridging hydride ligands on molecular geometry are maximized in *binuclear* species.

2. The Rh–ClB–Rh angles in the $Rh(\mu\text{-}Cl)_2Rh$ bridge are each 98.29 (3)–25.09 (7)° greater than the value of 73.20 (6)° found for the Rh–ClB–Rh angle in the $Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ bridge.

3. The angle defined at rhodium by the bridging ligands is 81.71 (3)° for ClB–Rh–ClB' and 91.6 (18)° for ClB–Rh–HB.

4. Neither the Rh–Cl(bridging) nor the Rh–Cl(terminal) distance is appreciably affected by the nature of the second

bridging ligand. Thus, in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$, Rh–ClT = 2.3967 (11) Å and Rh–ClB (average) = 2.4586 Å while Rh–ClT = 2.3929 (17) Å and Rh–ClB = 2.4374 (17) Å in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$.

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Registry No. $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$, 12354-85-7.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 2.[1] Direct Location of the μ_2-Hydride Ligand and Characterization of the 1,3-Dipolar $>C^-HCH_2P^+Me_2Ph$ Ligand in the $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ Molecule

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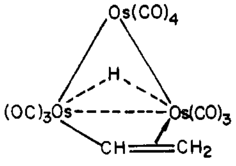
The species $HOs_3(CO)_{10}(C^-HCH_2P^+Me_2Ph)$, prepared previously from $HOs_3(CO)_{10}(CH{=}CH_2)$ and PMe_2Ph, has been studied via a single-crystal x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 11.3389 (18) Å, b = 16.4265 (25) Å, c = 13.8840 (20) Å, β = 100.64 (2)°, V = 2541.5 (7) Å^3, ρ(obsd) = 2.66 (1) g cm^{-3}, and ρ(calcd) = 2.657 g cm^{-3} for mol wt 1016.91 and Z = 4. Diffraction data were collected on a Picker FACS-1 automated diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement techniques. All atoms other than the methyl hydrogens were located, the final discrepancy indices being R_F = 3.61% and R_{wF} = 3.31% for the 3342 reliable reflections with $2\theta < 45°$ (Mo Kα radiation). The molecule contains a triangular arrangement of osmium atoms. Os(1) and Os(2) are each associated with three carbonyl ligands, while Os(3) is linked to four such ligands. In addition, Os(1) and Os(2) are mutually bridged by a hydride ligand (which was located and refined in the course of the structural analysis) and by a 1,3-dipolar $>C^-HCH_2P^+Me_2Ph$ ligand. Osmium–osmium bond lengths are Os(1)–Os(2) = 2.8002 (6) Å, Os(1)–Os(3) = 2.8688 (6) Å, and Os(2)–Os(3) = 2.8729 (6) Å. Since a single unsupported bridging hydride ligand normally causes an expansion in a metal–metal bond (relative to its value in an analogous nonbridged system), it follows that this effect is counterbalanced by a contrary bond-shortening influence of the bridging $>C^-HCH_2P^+Me_2Ph$ ligand in the present molecule. Osmium–(μ_2-hydride) distances are Os(1)–H = 1.95 (7) Å and Os(2)–H = 1.80 (8) Å; the angle Os(1)–H–Os(2) is 97 (3)°.

Introduction

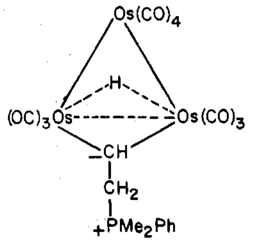
The complex $HOs_3(CO)_{10}(CH{=}CH_2)$ has been characterized[3,4] as having a vinyl group which bridges the edge of an Os_3 triangle in an unsymmetrical σ,π fashion (see I).



I

Shapley and co-workers originally investigated the reaction of I with organophosphines (:PR_3) with a view toward determining whether the coordinated double bond could be displaced by a suitable donor ligand. The product of the reaction of I with PMe_2Ph was found to be of the expected stoichiometry, viz., $HOs_3(CO)_{10}(CH{=}CH_2)\cdot PMe_2Ph$, but spectroscopic studies indicated that the incoming phosphine ligand attacked the coordinated double bond rather than its associated osmium atom.

A single-crystal x-ray structural analysis of this product was undertaken in order to obtain unambiguous information on its molecular stereochemistry (believed, correctly, to be as in II). The molecule is also of general relevance to our long-term



II

plan for structurally characterizing transition metal species